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(54) SEMICONDUCTOR PACKAGE WINDOW MATERIAL GLASS AND ITS FABRICATION METHOD

(57)Abstract:
PURPOSE: To prevent U and Th becoming a main source of á rays from being mixed into glass by restricting the amounts of contents of U and Th below specific values.
CONSTITUTION: In order to reduce radioisotopes contained in glass, it is necessary to restrict mixing-in of such radioisotopes in a glass manufacturing process except for careful selection of glass raw materials. For preventing radioisotopes from being mixed in a glass manufacturing process glass is melted under the condition where the entire or part of molten glass surface is prevented from making contact with the atmosphere in a melting furnace. The resulting glass contains 5ppb or less of U and 5ppb or less of Th. As a result, the amount of emission of á rays is not more than 0.0015C/cm2.hr, which is preferable as semiconductor package window material glass. Further, a soft error rate can be sharply reduced when it is used for a solid pickup device.

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JAPANESE [JP,08-306894,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] Aperture material glass for semiconductor packages characterized by both the contents of U and Th being 5 or less ppb.
[Claim 2] By weight %, aluminum 2O3 5 to 25% for B-2 O3 50 to 78% 0 - 8%, [SiO2] 0 - 18%, and K2O for Na2O 0 to 5% 0 - 20% [Li2O] (2O5 - 20% of however, Li2 O+Na2 O+K) Aperture material glass for semiconductor packages according to claim 1 which contains and consists of borosilicate glass whose coefficient of thermal expansion the content of the above-mentioned component is at least 80% or more, and is 45-75x10-7K-1.
[Claim 3] Aperture material glass for semiconductor packages according to claim 1 which contains 50 - 85%, and aluminum 2O3 for P2O5 4 to 20%, both sum total is 63% or more, and contains CuO 0.1 to 10% by weight %, and consists of near-infrared absorption glass whose coefficient of thermal expansion is 45-78x10-7K-1.
[Claim 4] The manufacture approach of the aperture material glass for semiconductor packages characterized by surface [of dissolution glass / all or some of] melting glass where contacting the ambient atmosphere in a fusion furnace is intercepted.
[Claim 5] (a) How to cover surface [in a fusion furnace / of melting glass / all or some of] by cutoff gas, (b) How to cover surface [in a fusion furnace / of melting glass / all or some of] with the lid made from a ceramic with few the products made from platinum and/or radioisotope contents, (c) — the approach using the fusion furnace with which the wall part in contact with the ambient atmosphere in a fusion furnace consists of platinum and/or ceramics with few radioisotope contents — since — the approach according to claim 4 of performing by at least one approach chosen.
[Claim 6] The method according to claim 4 or 5 of removing the surface layer of edges other than the polished surface of glass.
[Claim 7] The solid state image sensor which equips any 1 term of claims 1-3 with the aperture material glass for semiconductor packages of a publication, and grows into it.
[Claim 8] The solid state image sensor which equips any 1 term of claims 4-6 with the glass for semi-conductor aperture material obtained by the approach of a publication, and grows into it.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the glass used as aperture material for semiconductor packages, such as CCD (solid state image pickup device) used for a video camera etc., and its manufacture approach in detail about the aperture material glass for semiconductor packages, and its manufacture approach.
[0002]
[Description of the Prior Art] Since semi-conductors, such as CCD, produce a soft error by the alpha rays emitted from the aperture material for a package, reduction of the amount of the radioisotope which emits the alpha rays contained in the aperture material for a package is performed. As a radioisotope, although uranium (U), thorium (Th), and radium (Ra) are mentioned typically, since there is little abundance, Ra is not usually made an issue of, but U and Th are made into the problem. There are many alpha-rays burst sizes and especially U has them about 5 to 10 times compared with Th. [many] Therefore, especially reduction of the content of U is made important at reduction of the alpha-rays burst size in the circumference ingredient of a semi-conductor.
[0003] For the reason, some proposals have already accomplished for the purpose of reducing the amount of alpha rays irradiated by the solid state image pickup device. For example, the solid state image pickup device characterized by having formed in JP,3-74874,A the silicate glass thin film which contains lead in the sensor section, and intercepting a radiation is proposed. However, in manufacture of this solid state image pickup device, while the film production process of a silicate glass thin film is complicated and requiring long duration, it is cost high.
[0004] On the other hand, the glass with which the contents of radioisotope are below 100 or less ppb, and alpha-rays burst size 0.05 c/cm2 and hr, and purification separation of an alpha-rays radioactive element does not contain difficult Fe 2O3, and TiO2, PbO and ZrO2 in JP,5-275074,A is proposed, and the glass of the alpha-rays burst size 0.08 - 0.005 c/cm2, and hr is indicated by the example. Moreover, the low radiation glass which does not contain K2O leading to beta-rays generating in JP,6-211539,A excluding ZrO2 and BaO with many contents of U and Th, either is proposed, and the glass of the alpha-rays burst size 0.008 - 0.002 c/cm2, and hr is indicated by the example.
[0005]
[Problem(s) to be Solved by the Invention] However, in connection with the densification of a solid state image pickup device, the noise and soft error by alpha rays have been the failure of the still bigger improvement in image quality in recent years. The demand of reduction-izing of an alpha-rays burst size is still severer, and, recently, have come [therefore,] to let below 0.0015 c/cm2 and hr be targets. However, in order to attain this target, with the glass with which the content of U with many alpha-rays burst sizes exceeds 5ppb, it was substantially impossible.
[0006] By the way, when the aperture material glass for semiconductor packages is sealed with an alumina ceramic package, to be the ingredient which neither a crack nor distortion generates is demanded. The optical system of a color VTR camera consists of a lens system 1 to which image formation of the image is carried out, the quartz plates 2 and 3 which act as a low pass filter and the component 5 which stuck the near-infrared absorption filter 4 which has a correction-by-sensitiveness operation, and a solid state image pickup device 6, as shown in drawing 1 . A solid state image pickup device 6 sets to the alumina package 8 the CCD chip 7 in which the 3 color mosaic filter was formed to the light-receiving side, and has the composition of having pasted up on it the aperture material 9 for a glass package which is a light transmission member for protection with the epoxy resin etc. Therefore, it is required to adjust the coefficient of thermal expansion of the aperture material 9 for a glass package and the alumina ceramic package 8. The coefficient of thermal expansion of an alumina ceramic is usually in the range of 60-75x10-7K-1, and, as for the coefficient of thermal expansion of glass, it is desirable that it is the range of this, an EQC, and 45-75x10-7K-1 [small a little]. The sensibility field of CCD is covering the near-infrared ray range from the light region. Therefore, the sensibility which cuts the near-infrared part of incident light and is synthetically obtained using a near-infrared absorption filter was made to approximate to visibility, it is required to improve color repeatability, as shown in drawing 1 , the near-infrared absorption filter 4 is built into the component 5 between the quartz plate 2 of three sheets, and the quartz plate 3 of one sheet, there were many number of layerses which constitute a component 5, and there was a fault that the manufacturing cost was high.
[0007] Therefore, the object of this invention is (i). There are few contents of U and Th and they can control

generating of the soft error of a solid state image pickup device. (ii) which can contribute to improvement in image quality The alumina package and the coefficient of thermal expansion are adjusted. It has the advantage of excelling in sealing nature with an alumina package, and the need is accepted (iii). It has a correction-by-sensitiveness function simulataneously and is in offering the aperture material glass for semiconductor packages which also has the advantage of being able to attain the miniaturization of equipment, and cost reduction, and its manufacture approach.

[0008]

[Means for Solving the Problem] Until now, that to which the activity isotope contained in glass originates in the raw material of glass was considered to be most. However, when this invention person made glass as an experiment using the thing of a high grade with very few radioisotope contents as a raw material of glass, it found out that the radioisotope content of the obtained glass was still high level. That is, for reduction of the radioisotope contained in glass, it became clear that it was necessary to control mixing in a glass manufacture process besides selecting the raw material of glass carefully. And by melting glass, where it is intercepted as a concrete means to prevent mixing of the radioisotope in a glass manufacture process that surface [of fusion glass / all or some of] contacts the ambient atmosphere in a fusion furnace The obtained glass has U content of 5 or less ppb, and Th content of 5 or less ppb, as a result, the alpha-rays burst size became below 0.0015 c/cm2 and hr, and it found out that it was suitable as aperture material glass for semiconductor packages.

[0009] This invention is completed based on such knowledge, and both this inventions make a summary the manufacture approach of the aperture material glass for semiconductor packages characterized by melting glass where it is intercepted that all or some of aperture material glass for semiconductor packages characterized by the content of (I)U and Th being 5 or less ppb and surface (II) dissolution glass contact the ambient atmosphere in a fusion furnace.

[0010] (I) The aperture material glass for semiconductor packages of aperture material glass point ******** for semiconductor packages is explained.

[0011] The content of U and Th of both the aperture material glass for semiconductor packages of this invention is 5 or less ppb. As conventional aperture material glass for semiconductor packages, only that to which U content exceeds 5ppb is obtained, but the aperture material glass for semiconductor packages of this invention is new glass which did not exist conventionally at this point. As a result with very few contents of U and Th on both 5 or less ppb and very little aperture material glass for semiconductor packages of this invention, an alpha-rays burst size is very as low as below 0.0015 c/cm2 and hr, and when such a content of U and Th uses for a solid state image pickup device, it can reduce the rate of a soft error remarkably.

[0012] In the aperture material glass for semiconductor packages of this invention, both the contents of U and Th have 3 or less desirable ppb, and below 0.001 c/cm2 and hr of an alpha-rays burst size are desirable.

[0013] As an ingredient of the aperture material glass for semiconductor packages of this invention, borosilicate glass or CuO is contained and the near-infrared absorption glass which uses P2O5-aluminum 2O3 as the base is mentioned.

[0014] The above-mentioned borosilicate glass which is one mode of the glass ingredient of this invention Preferably B-2 O3 50 to 78% for SiO2 by weight % 5 - 25%, 0 - 18%, and K2O for Na2O 0 to 5% 0 to 8% 0 - 20% [aluminum 2O3] [Li2O] (2O5 - 20% of however, Li2 O+Na2 O+K) It contains, the content of the above-mentioned component is at least 80% or more, and that whose coefficient of thermal expansion is 45-75x10-7K-1 is desirable.

[0015] The operation of each component and the reason for presentation definition in this borosilicate glass are explained below.

[0016] SiO2 and B-2 O3 are components which make the frame of borosilicate glass. SiO2 becomes less than 50%, and when B-2 O3 exceeds 25%, there is an inclination for weatherability to fall. Moreover, SiO2 exceeds 78% and there is an inclination for fusion nature to get worse [B-2 O3] at less than 5%. Therefore, SiO2 is in 50 - 78% of range, and it is suitable for B-2 O3 that it is 5 - 25% of range.

[0017] aluminum 2O3 is a component which raises the weatherability of glass. However, when 8% is exceeded, the inclination a stria becomes easy to generate is in glass. Therefore, considering as 8% or less is appropriate for the content of aluminum 2O3.

[0018] Li2O, Na2O, and K2O are components which act as a fusing agent and improve devitrification-proof nature. For that purpose, 5% or more of the content of one sort or two sorts or more of sum totals of these components is suitable. However, there is an inclination for weatherability to worsen if the content of one sort or two sorts or more of sum totals of these components exceeds 20%, and for a coefficient of thermal expansion to change too much greatly. Among these components, when it adds so much, the operation of Li2O which there is an inclination for devitrification-proof nature to get worse, and corrodes the container of refractories is also still stronger. Therefore, as for the content of Li2O, it is desirable to make it to 5% or less. Na2O and K2O have the inclination for weatherability to get worse if 18% and 20% are exceeded, respectively, and for a coefficient of thermal expansion to also become large too much. Therefore, as for the content of Na2O and K2O, it is desirable to consider as 18% or less and 20% or less, respectively.

[0019] It is less than 20% of range for the object other than the above component, such as an improvement of weatherability, fusion nature, and devitrification-proof nature, and adjustment of a coefficient of thermal expansion, and it is also possible to add halogens, such as an alkaline-earth-metal oxide (MgO, CaO, SrO, BaO), and ZnO, Cl, etc. Furthermore, the defoaming agent of As 2O3 and Sb2O3 grade can also be added suitably if needed. Moreover,

the high valence metallic oxide more than trivalent [other] can also be added to extent which does not spoil a desired property.

[0020] The near-infrared absorption glass which is another mode of this invention glass ingredient and which contains CuO and uses P2O5-aluminum 2O3 as the base It is weight % preferably, and 50 - 85% and aluminum 2O3 are contained for P2O5 4 to 20%, both sum total is 63% or more, and CuO is contained 0.1 to 10%, and that whose coefficient of thermal expansion is 45-75x10-7K-1 is desirable. If the near-infrared absorption glass of this CuO content and the 2OP2O5-aluminum3 base is used as aperture material glass for semiconductor packages, it can be made to serve also as the function as a near-infrared absorption filter. That is, as drawing 2 showed, as aperture material glass for a package, by using the near-infrared absorption glass 11 which adjusted the coefficient of thermal expansion and coefficient of thermal expansion of the alumina ceramic package 8, as shown in drawing 1 , the near-infrared absorption filter 4 did not need to be formed between the quartz plate 2 and the quartz plate 3, and a miniaturization and cost cut of a product were attained.

[0021] An operation of each component of this near-infrared absorption glass and the reason for presentation definition are explained below.

[0022] P2O5 have the high permeability of the light, and in order that the cut nature of near-infrared light may be good and may obtain glass suitable as an object for correction by sensitiveness, they are an indispensable component. However, since volatilization will also become intense and fusion will become difficult while there is an inclination for the viscosity of glass to become high too much if 85% is exceeded, an upper limit is 80% preferably 85%. On the other hand, since there is an inclination for a coefficient of thermal expansion to become [P2O5] large too much at less than 50%, a minimum is 55% preferably 50%.

[0023] aluminum 2O3 is a component especially effective for improving chemical durability. However, at less than 4%, when the effectiveness is not enough and exceeds 20%, there is an inclination for devitrification-proof nature to get worse. Then, a minimum is 7% preferably 4%, and an upper limit is 15% preferably 20%.

[0024] The content of CuO is 0.1 - 6% preferably 0.1 to 10%. Although CuO is effective in a near-infrared light cut, when there is little the effectiveness and it exceeds 10%, at less than 0.1%, there is an inclination for the permeability of the light to get worse with devitrification-proof nature.

[0025] Furthermore, the content of B-2 O3 is 0 - 15%, and the content of SiO2 is 0 - 25%. One sort or two sorts or more of contents of a group which consist of MgO, CaO, SrO(s), BaO(s), and ZnO(s) are 0 - 25%. One sort or two sorts or more of contents of a group which consist of B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO are 5 - 37%. And it is desirable that the sum total of the content of a group which consists of P2O5, aluminum2O3, and B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO is 85% or more.

[0026] SiO2 and B-2 O3 are effective in reducing an improvement and coefficient of thermal expansion of devitrification-proof nature. However, SiO2 will become ****** if 25% is exceeded, and as for B-2 O3, when 15% is exceeded, it has the inclination to worsen devitrification-proof nature.

[0027] MgO, CaO, SrO, BaO, and ZnO are effective in the improvement of fusion nature, or the improvement of devitrification-proof nature. However, if 25% is exceeded, a coefficient of thermal expansion will become large too much, and it becomes difficult to obtain a desired coefficient of thermal expansion.

[0028] Furthermore, it is appropriate for the total amount of a group which consists of B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO to consider as 6 - 30% of range preferably 5 to 37% from a viewpoint of fusion nature, devitrification-proof nature, a coefficient of thermal expansion, and a transparency property.

[0029] Moreover, it is suitable for the sum total of the content of a group which consists of P2O5, aluminum2O3, and B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO from the same reason that it is 90% or more preferably 85% or more. In addition to the above-mentioned component, it is also possible to be less than 10% of range preferably, and to contain Sb 2O3, Nb2O5, PbO and La 2O3, an alkali-metal oxide, etc. less than 15%, for the purpose of the improvement of weatherability, fusion nature, devitrification-proof nature, etc., adjustment of a coefficient of thermal expansion, etc.

[0030] Which gestalten, such as a water solution, a carbonate, a nitrate, a hydroxide, and an oxide, are sufficient as the raw material for forming the above-mentioned borosilicate glass and CuO content, and P2O5-aluminum2O3 base glass. However, it is necessary to choose a raw material with few [as mentioned above] contents of U and Th which are mixed as an impurity.

[0031] (II) The manufacture approach of the aperture material glass for semiconductor packages of manufacture approach this invention of the aperture material glass for semiconductor packages is characterized by fusing glass, where it is intercepted that all or some of fusion glass front faces contact the ambient atmosphere in a fusion furnace.

[0032] As an approach for intercepting, that surface [of fusion glass / all or some of] contacts the ambient atmosphere in a fusion furnace (a) How to cover surface [in a fusion furnace / of fusion glass / all or some of] by cutoff gas, (b) How to cover surface [in a fusion furnace / of fusion glass / all or some of] with the lid made from a ceramic with few the products made from platinum and/or radioisotope contents, (c) by adopting the approach above-mentioned approach (a) using the fusion furnace with which the wall part in contact with the ambient atmosphere in a fusion furnace consists of platinum and/or ceramics with few radioisotope contents, (b), or (c) The reason glass with very few U and Th contents is obtained is guessed as follows. That is, in dissolution actuation of glass, although especially the steam of U occurs, if all or some of glass front faces intercept radioisotope and contacting the ambient atmosphere in a fusion furnace by at least one of the above-mentioned approach (a) - (c) from the brick which constitutes the wall of a fusion furnace, or a heating element (for example, a silicon carbide

sintered compact and a molybdenum silicide sintered compact), it will be prevented that U steam mixes into glass.
[0033] The approach of this invention may be performed by adopting either the above-mentioned approach (a), (b) and (c), and may use together the above-mentioned approach (a) or an approach (b), and an approach (c).
[0034] Although it can prevent that glass and a fusion furnace ambient atmosphere contact as cutoff gas used by the above-mentioned approach (a), and the class will not be asked to glass if substantially inactive, hydrocarbon gas, such as N2, Ar, air, carbon dioxide gas, and CH4, LNG, etc. can be used, for example.
[0035] Although it is desirable to use the muffle furnace which constituted the wall from a ceramic with few radioisotope contents as for the fusion furnace used in the above-mentioned approach (c), you may not necessarily be muffle structure, and it is effective even if it constitutes the walls (head lining, side attachment wall, etc.) of the usual fusion furnace from a ceramic with few radioisotope contents. As these ceramics, 20 ppm or less of U contents are preferably suitable for the nature electrocast brick of an alumina 1 ppm or less, a silica block, etc. Moreover, the activity of resistance heating elements, such as a silicon carbide sintered compact and a molybdenum silicide sintered compact, is controlled, and gas heating of LNG etc. is desirable.
[0036] In the manufacture approach of the aperture material glass for semiconductor packages of this invention, the amount of Th can be further decreased by removing the surface layer of end faces other than the polished surface which counters. It is as follows when this point is described in detail. That is, although edges other than the polished surface which counters are usually a cutting plane or a rough ZURI side in case polish processing of the glass is carried out at the aperture material for a package, CeO2 of an abrasive material fixes to the cutting plane or a rough ZURI side, and ThO2 which is an impurity in CeO2 becomes a source of alpha rays by remaining without being washed. Then, it can prevent CeO2 fixing during polish by graduating the concavo-convex section of an edge in advance by acid treatment etc. Moreover, acid treatment etc. may remove the surface layer of an edge after polish.
[0037] As mentioned above, although the characteristic requirements for the manufacture approach of the aperture material glass for semiconductor packages of this invention have been explained, in order for both U and Th content to obtain glass of 5 or less ppb, of course, consideration which uses few [as much as possible] high grade raw materials of a radioisotope content, and radioisotope does not mix as much as possible in mixing of a raw material and migration to a fusion furnace must be carried out as the premise.
[0038]
[Example] An example explains this invention in more detail below.
[0039] (Example 1) Various high grade raw materials were used, and the raw material batch was produced so that it might become the presentation of a table 1 of No.1. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.8ppb and 3.2ppb, respectively. It melted and refined in 1480 degrees C and 8 hours, having put this raw material batch (it being 10kg by oxide conversion) into the crucible made from platinum of 5l. capacity, having flowed N2 gas by the flow rate of 40l. / min all over the kanthal super furnace (molybdenum silicide heating element activity), and intercepting raw materials for glass with a fusion furnace ambient atmosphere (degassing, homogenization). It cast to the iron metal flask, predetermined annealing was carried out, and the glass block (henceforth Glass A) was obtained. When U of this glass A and Th content were analyzed using TCP-MASS by YOKOGAWA ELECTRIC CORP., it was 2.5ppb and 3.4ppb, respectively, and both U and Th content were 5 or less ppb.
[0040] (Example 1 of a comparison) Except not carrying out the inflow of N2 gas, it is the same conditions as an example 1, and the glass block (henceforth comparison glass V) was obtained similarly. U of this comparison glass V and Th content were 42ppb and 3.6ppb, respectively, and its U content was remarkably high compared with the example 1.
[0041] From the result of an example 1 and the example 1 of a comparison, it became clear by N2 gas's permuting a furnace atmosphere and intercepting glass from a furnace atmosphere that U content could be decreased notably.
[0042] (Example 2) The raw material batch was produced using the high grade raw material so that it might become the presentation of a table 1 of No.4. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.2ppb and 0.1ppb, respectively. As shown in drawing 3 for the heating dissolution of glass, it consisted of outer wall material 12 and a silicon carbide heating element 13, the wall 14 was divided with the silica block, and the electric furnace 15 made into muffle structure was used. The contents of U and Th of the outer wall material 12 (nature brick of a chamotte) of a wall 14 (silica block) and an electric furnace were U:19ppb, Th:0.1ppb and U:30 ppm, and Th:55ppm, respectively. The crucible made from platinum of 1l. capacity was used, it melted, the raw material batch (it is 2kg by oxide conversion) was refined in 1430 degrees C and 6 hours, it cast to the iron metal flask, predetermined annealing was carried out, and the glass block (henceforth Glass B) was obtained. When this glass B was analyzed, the contents of U and Th were 1.2ppb and 0.2ppb, respectively.
[0043] (Example 2 of a comparison) Except having used the electric furnace which removed the wall of the silica block 14 of drawing 3 , it is the same conditions as an example 2, and the glass block (henceforth comparison glass W) was obtained similarly. The analysis values of U and Th of this comparison glass W were 18ppb and 0.3ppb, respectively.
[0044] From the result of an example 2 and the example 2 of a comparison, it became clear by constituting the part in contact with a furnace atmosphere from an ingredient with few radioisotope contents, and intercepting glass from a furnace atmosphere that U content in glass could be decreased.

[0045] (Example 3) Polish processing of the glass A obtained in the example 1 was carried out by the usual approach, and the aperture material glass for a package (henceforth Glass C) of a predetermined configuration (15.5x17.7x0.8mm) was produced. Although 15.5x17.7mm side of this glass C is a ground field, 15.5x0.8mm side and 17.7x0.8mm side are cutting planes which had the angle beveled. After having applied the protective coat to the polished surface, being immersed in the fluoric acid water solution and etching only an end face, the protective coat was removed and glass (henceforth Glass D) was obtained. U of the glass C before etching and Th analysis value were U:2.5ppb and Th:5.8ppb, respectively, and U of the glass D after etching and Th analysis value were U:2.3ppb and Th:3.8ppb, respectively. That is, it became clear by removing the rough ZURI side of an edge that Th of a polish article could be decreased.
[0046] (Example 4) Various high grade raw materials were used so that it might become the presentation of a table 2 of No.1, and the raw material batch was produced. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.7ppb and 0.4ppb, respectively. With the muffle furnace of drawing 3 , it rough-melted in 1350 degrees C and 3 hours using the silica crucible of 7l. capacity, and it melted and it was refined in 1350 more degrees C and 5 hours after moving and changing this raw material batch (it is 12kg by oxide conversion) into the crucible made from platinum of 5l. capacity. It cast to the iron metal flask, predetermined annealing was carried out, and the glass block was obtained. After carrying out polish processing of this glass with a conventional method, the end face was removed like the example 3 and the 15.5x17.7x2.0mm aperture material glass for a package (henceforth Glass E) was obtained. The analysis values of U and Th of this glass E were 1.9ppb and 0.8ppb, respectively. Moreover, the spectral transmittance of this glass E had the near-infrared light cut property suitable as an object for CCD correction by sensitiveness, as shown in drawing 4 .
[0047] (Example of a trial) Epoxy resin adhesive was used and sealed using the polish plate and Glass D, and E itself which carried out polish processing with the conventional method, and obtained Glass A and B as aperture material glass for a package in the alumina ceramic package which contained the CCD chip of 580,000 pixels of effective pixel numbers for these, and the solid state image pickup device was produced.
[0048] The solid state image pickup device was similarly produced using the glass which carried out polish processing with the conventional method, and obtained the commercial aperture material glass for a package (henceforth comparison glass X) as aperture material glass for a package for the comparison.
[0049] In addition, although it was going to produce to the solid state image pickup device using the commercial near-infrared absorption glass for correction by sensitiveness (it is called FUTSU phosphate glass and following comparison glass Y), this comparison glass Y had the coefficient of thermal expansion as large as 158x10-7K-1, and when it was sealing, the crack occurred and it was not able to obtain a solid state image pickup device.
[0050] Next, these obtained solid state image pickup devices were used, and the existence of a soft error was investigated. The result is shown in a table 3. In addition, the alpha-rays burst size was measured among the table with the alpha-rays measuring device LACS by the Sumitomo analysis pin center,large company. When using the glass by this invention so that clearly from a table 3, it became clear that a soft error could be reduced greatly.
[0051] It cannot be overemphasized that this invention is not limited to the above-mentioned example, and various variations may exist as mentioned above.
[0052] A weight % display shows the various glass presentations which can be used for a table 1 and a table 2 in this invention. A coefficient of thermal expansion is the measured value by the TMA analysis apparatus among a table. All have the coefficient of thermal expansion which suited sealing with an alumina ceramic.
[0053]
[A table 1]

（ホウケイ酸ガラス）

No.	1	2	3	4	5	6	7	8
SiO_2	69.4	65.4	69.4	59.0	67.8	67.3	61.4	74.5
B_2O_3	17.6	17.6	15.0	20.0	15.8	15.8	17.8	6.3
Al_2O_3	3.6	3.6		3.0	2.5	3.1	1.6	6.6
Li_2O	0.7	0.7						
Na_2O	0.7	0.7	10.0		4.3	10.7		6.2
K_2O	8.0	8.0	1.6	15.4	8.1		7.2	1.3
BaO					1.3			5.1
ZnO		4.0	4.0	2.6	0.2	3.1	10.0	
NaCl							2.0	
Sb_2O_3	1.0	1.0	0.4	0.2	0.2	0.2		0.4
熱膨張係数 ($\times10^{-7}K^{-1}$)	48	50	67	72	65	64	47	55

[0054]
[A table 2]

(CuO含有、P_2O_5−Al_2O_3ベースガラス)

No.	1	2	3	4	5	6	7
P_2O_5	76.3	71.4	77.7	73.2	80.5	57.0	65.0
Al_2O_3	14.5	9.0	15.0	12.1	7.7	15.0	15.0
B_2O_3	1.0					5.0	10.0
SiO_2					5.2	23.0	10.0
MgO	5.2	4.5	4.3				
CaO				6.7			
SrO				2.0			
BaO		5.3	3.0		6.6		
ZnO	1.0	8.0					
Sb_2O_3				6.0			
Nb_2O_5		1.8					
CuO	2.0	2.6	4.0	1.0	0.6	0.6	0.4
熱膨張係数 ($x10^{-7}K^{-1}$)	67	68	62	69	72	52	57

[0055]
[A table 3]

	U 量 (ppb)	Th量 (ppb)	α線放出量 (c/cm²·hr)	ソフトエラー
ガラス A	2.6	3.4	< 0.0015	少ない
ガラス B	1.2	0.2	< 0.0015	少ない
ガラス C	2.3	3.8	< 0.0015	少ない
ガラス D	1.9	0.8	< 0.0015	少ない
比較ガラスV	42	3.6	0.004	非常に多い
比較ガラスW	18	0.3	0.002	非常に多い
比較ガラスX	12	13	0.002	多い
比較ガラスY	210	93	0.02	—

[0056]
[Effect of the Invention] According to this invention, the glass for package aperture material for semi-conductors, such as a solid state image pickup device with it, can be offered. [the remarkable rate of a soft error and] [low] Furthermore, an alumina ceramic package and glass with the good coefficient of thermal expansion of junction nature can be offered by limiting to the specific presentation range. According to the manufacture approach of the glass of this invention, mixing of U and Th in a production process can be controlled substantially, and the glass suitable for the aperture material for a package can be obtained, and since generating of the soft error which originates in alpha rays from glass can be reduced remarkably, it can contribute to high-resolution-izing of semi-conductors, such as a solid state image pickup device, and densification. Moreover, if infrared absorbing glass with a correction-by-sensitiveness function is used as aperture material for a package, the miniaturization of CCD is possible and cost reduction can also be expected.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the glass used as aperture material for semiconductor packages, such as CCD (solid state image pickup device) used for a video camera etc., and its manufacture approach in detail about the aperture material glass for semiconductor packages, and its manufacture approach.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Since semi-conductors, such as CCD, produce a soft error by the alpha rays emitted from the aperture material for a package, reduction of the amount of the radioisotope which emits the alpha rays contained in the aperture material for a package is performed. As a radioisotope, although uranium (U), thorium (Th), and radium (Ra) are mentioned typically, since there is little abundance, Ra is not usually made an issue of, but U and Th are made into the problem. There are many alpha-rays burst sizes and especially U has them about 5 to 10 times compared with Th. [many] Therefore, especially reduction of the content of U is made important at reduction of the alpha-rays burst size in the circumference ingredient of a semi-conductor.
[0003] For the reason, some proposals have already accomplished for the purpose of reducing the amount of alpha rays irradiated by the solid state image pickup device. For example, the solid state image pickup device characterized by having formed in JP,3-74874,A the silicate glass thin film which contains lead in the sensor section, and intercepting a radiation is proposed. However, in manufacture of this solid state image pickup device, while the film production process of a silicate glass thin film is complicated and requiring long duration, it is cost high.
[0004] On the other hand, the glass with which the contents of radioisotope are below 100 or less ppb, and alpha-rays burst size 0.05 c/cm2 and hr, and purification separation of an alpha-rays radioactive element does not contain difficult Fe 2O3, and TiO2, PbO and ZrO2 in JP,5-275074,A is proposed, and the glass of the alpha-rays burst size 0.08 - 0.005 c/cm2, and hr is indicated by the example. Moreover, the low radiation glass which does not contain K2O leading to beta-rays generating in JP,6-211539,A excluding ZrO2 and BaO with many contents of U and Th, either is proposed, and the glass of the alpha-rays burst size 0.008 - 0.002 c/cm2, and hr is indicated by the example.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the glass for package aperture material for semi-conductors, such as a solid state image pickup device with it, can be offered. [the remarkable rate of a soft error and] [low] Furthermore, an alumina ceramic package and glass with the good coefficient of thermal expansion of junction nature can be offered by limiting to the specific presentation range. According to the manufacture approach of the glass of this invention, mixing of U and Th in a production process can be controlled substantially, and the glass suitable for the aperture material for a package can be obtained, and since generating of the soft error which originates in alpha rays from glass can be reduced remarkably, it can contribute to high-resolution-izing of semi-conductors, such as a solid state image pickup device, and densification. Moreover, if infrared absorbing glass with a correction-by-sensitiveness function is used as aperture material for a package, the miniaturization of CCD is possible and cost reduction can also be expected.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in connection with the densification of a solid state image pickup device, the noise and soft error by alpha rays have been the failure of the still bigger improvement in image quality in recent years. The demand of reduction-izing of an alpha-rays burst size is still severer, and, recently, have come [therefore,] to let below 0.0015 c/cm2 and hr be targets. However, in order to attain this target, with the glass with which the content of U with many alpha-rays burst sizes exceeds 5ppb, it was substantially impossible.

[0006] By the way, when the aperture material glass for semiconductor packages is sealed with an alumina ceramic package, to be the ingredient which neither a crack nor distortion generates is demanded. The optical system of a color VTR camera consists of a lens system 1 to which image formation of the image is carried out, the quartz plates 2 and 3 which act as a low pass filter and the component 5 which stuck the near-infrared absorption filter 4 which has a correction-by-sensitiveness operation, and a solid state image pickup device 6, as shown in drawing 1 . A solid state image pickup device 6 sets to the alumina package 8 the CCD chip 7 in which the 3 color mosaic filter was formed to the light-receiving side, and has the composition of having pasted up on it the aperture material 9 for a glass package which is a light transmission member for protection with the epoxy resin etc. Therefore, it is required to adjust the coefficient of thermal expansion of the aperture material 9 for a glass package and the alumina ceramic package 8. The coefficient of thermal expansion of an alumina ceramic is usually in the range of 60-75x10-7K-1, and, as for the coefficient of thermal expansion of glass, it is desirable that it is the range of this, an EQC, and 45-75x10-7K-1 [small a little]. The sensibility field of CCD is covering the near-infrared ray range from the light region. Therefore, the sensibility which cuts the near-infrared part of incident light and is synthetically obtained using a near-infrared absorption filter was made to approximate to visibility, it is required to improve color repeatability, as shown in drawing 1 , the near-infrared absorption filter 4 is built into the component 5 between the quartz plate 2 of three sheets, and the quartz plate 3 of one sheet, there were many number of layerses which constitute a component 5, and there was a fault that the manufacturing cost was high.

[0007] Therefore, the object of this invention is (i). There are few contents of U and Th and they can control generating of the soft error of a solid state image pickup device. (ii) which can contribute to improvement in image quality The alumina package and the coefficient of thermal expansion are adjusted. It has the advantage of excelling in sealing nature with an alumina package, and the need is accepted (iii). It has a correction-by-sensitiveness function simulataneously and is in offering the aperture material glass for semiconductor packages which also has the advantage of being able to attain the miniaturization of equipment, and cost reduction, and its manufacture approach.

[Translation done.]

MEANS

[Means for Solving the Problem] Until now, that to which the activity isotope contained in glass originates in the raw material of glass was considered to be most. However, when this invention person made glass as an experiment using the thing of a high grade with very few radioisotope contents as a raw material of glass, it found out that the radioisotope content of the obtained glass was still high level. That is, for reduction of the radioisotope contained in glass, it became clear that it was necessary to control mixing in a glass manufacture process besides selecting the raw material of glass carefully. And by melting glass, where it is intercepted as a concrete means to prevent mixing of the radioisotope in a glass manufacture process that surface [of fusion glass / all or some of] contacts the ambient atmosphere in a fusion furnace The obtained glass has U content of 5 or less ppb, and Th content of 5 or less ppb, as a result, the alpha-rays burst size became below 0.0015 c/cm2 and hr, and it found out that it was suitable as aperture material glass for semiconductor packages.
[0009] This invention is completed based on such knowledge, and both this inventions make a summary the manufacture approach of the aperture material glass for semiconductor packages characterized by melting glass where it is intercepted that all or some of aperture material glass for semiconductor packages characterized by the content of (I)U and Th being 5 or less ppb and surface (II) dissolution glass contact the ambient atmosphere in a fusion furnace.
[0010] (I) The aperture material glass for semiconductor packages of aperture material glass point ******** for semiconductor packages is explained.
[0011] The content of U and Th of both the aperture material glass for semiconductor packages of this invention is 5 or less ppb. As conventional aperture material glass for semiconductor packages, only that to which U content exceeds 5ppb is obtained, but the aperture material glass for semiconductor packages of this invention is new glass which did not exist conventionally at this point. As a result with very few contents of U and Th on both 5 or less ppb and very little aperture material glass for semiconductor packages of this invention, an alpha-rays burst size is very as low as below 0.0015 c/cm2 and hr, and when such a content of U and Th uses for a solid state image pickup device, it can reduce the rate of a soft error remarkably.
[0012] In the aperture material glass for semiconductor packages of this invention, both the contents of U and Th have 3 or less desirable ppb, and below 0.001 c/cm2 and hr of an alpha-rays burst size are desirable.
[0013] As an ingredient of the aperture material glass for semiconductor packages of this invention, borosilicate glass or CuO is contained and the near-infrared absorption glass which uses P2O5-aluminum 2O3 as the base is mentioned.
[0014] The above-mentioned borosilicate glass which is one mode of the glass ingredient of this invention Preferably B-2 O3 50 to 78% for SiO2 by weight % 5 - 25%, 0 - 18%, and K2O for Na2O 0 to 5% 0 to 8% 0 - 20% [aluminum 2O3] [Li2O] (2O5 - 20% of however, Li2 O+Na2 O+K) It contains, the content of the above-mentioned component is at least 80% or more, and that whose coefficient of thermal expansion is 45-75x10-7K-1 is desirable.
[0015] The operation of each component and the reason for presentation definition in this borosilicate glass are explained below.
[0016] SiO2 and B-2 O3 are components which make the frame of borosilicate glass. SiO2 becomes less than 50%, and when B-2 O3 exceeds 25%, there is an inclination for weatherability to fall. Moreover, SiO2 exceeds 78% and there is an inclination for fusion nature to get worse [B-2 O3] at less than 5%. Therefore, SiO2 is in 50 - 78% of range, and it is suitable for B-2 O3 that it is 5 - 25% of range.
[0017] aluminum 2O3 is a component which raises the weatherability of glass. However, when 8% is exceeded, the inclination a stria becomes easy to generate is in glass. Therefore, considering as 8% or less is appropriate for the content of aluminum 2O3.
[0018] Li2O, Na2O, and K2O are components which act as a fusing agent and improve devitrification-proof nature. For that purpose, 5% or more of the content of one sort or two sorts or more of sum totals of these components is suitable. However, there is an inclination for weatherability to worsen if the content of one sort or two sorts or more of sum totals of these components exceeds 20%, and for a coefficient of thermal expansion to change too much greatly. Among these components, when it adds so much, the operation of Li2O which there is an inclination for devitrification-proof nature to get worse, and corrodes the container of refractories is also still stronger. Therefore, as for the content of Li2O, it is desirable to make it to 5% or less. Na2O and K2O have the inclination for weatherability to get worse if 18% and 20% are exceeded, respectively, and for a coefficient of thermal

expansion to also become large too much. Therefore, as for the content of Na2O and K2O, it is desirable to consider as 18% or less and 20% or less, respectively.
[0019] It is less than 20% of range for the object other than the above component, such as an improvement of weatherability, fusion nature, and devitrification-proof nature, and adjustment of a coefficient of thermal expansion, and it is also possible to add halogens, such as an alkaline-earth-metal oxide (MgO, CaO, SrO, BaO), and ZnO, Cl, etc. Furthermore, the defoaming agent of As 2O3 and Sb2O3 grade can also be added suitably if needed. Moreover, the high valence metallic oxide more than trivalent [other] can also be added to extent which does not spoil a desired property.
[0020] The near-infrared absorption glass which is another mode of this invention glass ingredient and which contains CuO and uses P2O5-aluminum 2O3 as the base It is weight % preferably, and 50 - 85% and aluminum 2O3 are contained for P2O5 4 to 20%, both sum total is 63% or more, and CuO is contained 0.1 to 10%, and that whose coefficient of thermal expansion is 45-75x10-7K-1 is desirable. If the near-infrared absorption glass of this CuO content and the 2OP2O5-aluminum3 base is used as aperture material glass for semiconductor packages, it can be made to serve also as the function as a near-infrared absorption filter. That is, as drawing 2 showed, as aperture material glass for a package, by using the near-infrared absorption glass 11 which adjusted the coefficient of thermal expansion and coefficient of thermal expansion of the alumina ceramic package 8, as shown in drawing 1 , the near-infrared absorption filter 4 did not need to be formed between the quartz plate 2 and the quartz plate 3, and a miniaturization and cost cut of a product were attained.
[0021] An operation of each component of this near-infrared absorption glass and the reason for presentation definition are explained below.
[0022] P2O5 have the high permeability of the light, and in order that the cut nature of near-infrared light may be good and may obtain glass suitable as an object for correction by sensitiveness, they are an indispensable component. However, since volatilization will also become intense and fusion will become difficult while there is an inclination for the viscosity of glass to become high too much if 85% is exceeded, an upper limit is 80% preferably 85%. On the other hand, since there is an inclination for a coefficient of thermal expansion to become [P2O5] large too much at less than 50%, a minimum is 55% preferably 50%.
[0023] aluminum 2O3 is a component especially effective for improving chemical durability. However, at less than 4%, when the effectiveness is not enough and exceeds 20%, there is an inclination for devitrification-proof nature to get worse. Then, a minimum is 7% preferably 4%, and an upper limit is 15% preferably 20%.
[0024] The content of CuO is 0.1 - 6% preferably 0.1 to 10%. Although CuO is effective in a near-infrared light cut, when there is little the effectiveness and it exceeds 10%, at less than 0.1%, there is an inclination for the permeability of the light to get worse with devitrification-proof nature.
[0025] Furthermore, the content of B-2 O3 is 0 - 15%, and the content of SiO2 is 0 - 25%. One sort or two sorts or more of contents of a group which consist of MgO, CaO, SrO(s), BaO(s), and ZnO(s) are 0 - 25%. One sort or two sorts or more of contents of a group which consist of B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO are 5 - 37%. And it is desirable that the sum total of the content of a group which consists of P2O5, aluminum2O3, and B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO is 85% or more.
[0026] SiO2 and B-2 O3 are effective in reducing an improvement and coefficient of thermal expansion of devitrification-proof nature. However, SiO2 will become ****** if 25% is exceeded, and as for B-2 O3, when 15% is exceeded, it has the inclination to worsen devitrification-proof nature.
[0027] MgO, CaO, SrO, BaO, and ZnO are effective in the improvement of fusion nature, or the improvement of devitrification-proof nature. However, if 25% is exceeded, a coefficient of thermal expansion will become large too much, and it becomes difficult to obtain a desired coefficient of thermal expansion.
[0028] Furthermore, it is appropriate for the total amount of a group which consists of B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO to consider as 6 - 30% of range preferably 5 to 37% from a viewpoint of fusion nature, devitrification-proof nature, a coefficient of thermal expansion, and a transparency property.
[0029] Moreover, it is suitable for the sum total of the content of a group which consists of P2O5, aluminum2O3, and B-2s O3, SiO2, MgO, CaO, SrO, BaO, and ZnO from the same reason that it is 90% or more preferably 85% or more. In addition to the above-mentioned component, it is also possible to be less than 10% of range preferably, and to contain Sb 2O3, Nb2O5, PbO and La 2O3, an alkali-metal oxide, etc. less than 15%, for the purpose of the improvement of weatherability, fusion nature, devitrification-proof nature, etc., adjustment of a coefficient of thermal expansion, etc.
[0030] Which gestalten, such as a water solution, a carbonate, a nitrate, a hydroxide, and an oxide, are sufficient as the raw material for forming the above-mentioned borosilicate glass and CuO content, and P2O5-aluminum2O3 base glass. However, it is necessary to choose a raw material with few [as mentioned above] contents of U and Th which are mixed as an impurity.
[0031] (II) The manufacture approach of the aperture material glass for semiconductor packages of manufacture approach this invention of the aperture material glass for semiconductor packages is characterized by fusing glass, where it is intercepted that all or some of fusion glass front faces contact the ambient atmosphere in a fusion furnace.
[0032] As an approach for intercepting, that surface [of fusion glass / all or some of] contacts the ambient atmosphere in a fusion furnace (a) How to cover surface [in a fusion furnace / of fusion glass / all or some of] by cutoff gas, (b) How to cover surface [in a fusion furnace / of fusion glass / all or some of] with the lid made from a ceramic with few the products made from platinum and/or radioisotope contents, (c) by adopting the approach

above-mentioned approach (a) using the fusion furnace with which the wall part in contact with the ambient atmosphere in a fusion furnace consists of platinum and/or ceramics with few radioisotope contents, (b), or (c) The reason glass with very few U and Th contents is obtained is guessed as follows. That is, in dissolution actuation of glass, although especially the steam of U occurs, if all or some of glass front faces intercept radioisotope and contacting the ambient atmosphere in a fusion furnace by at least one of the above-mentioned approach (a) - (c) from the brick which constitutes the wall of a fusion furnace, or a heating element (for example, a silicon carbide sintered compact and a molybdenum silicide sintered compact), it will be prevented that U steam mixes into glass.
[0033] The approach of this invention may be performed by adopting either the above-mentioned approach (a), (b) and (c), and may use together the above-mentioned approach (a) or an approach (b), and an approach (c).
[0034] Although it can prevent that glass and a fusion furnace ambient atmosphere contact as cutoff gas used by the above-mentioned approach (a), and the class will not be asked to glass if substantially inactive, hydrocarbon gas, such as N2, Ar, air, carbon dioxide gas, and CH4, LNG, etc. can be used, for example.
[0035] Although it is desirable to use the muffle furnace which constituted the wall from a ceramic with few radioisotope contents as for the fusion furnace used in the above-mentioned approach (c), you may not necessarily be muffle structure, and it is effective even if it constitutes the walls (head lining, side attachment wall, etc.) of the usual fusion furnace from a ceramic with few radioisotope contents. As these ceramics, 20 ppm or less of U contents are preferably suitable for the nature electrocast brick of an alumina 1 ppm or less, a silica block, etc. Moreover, the activity of resistance heating elements, such as a silicon carbide sintered compact and a molybdenum silicide sintered compact, is controlled, and gas heating of LNG etc. is desirable.
[0036] In the manufacture approach of the aperture material glass for semiconductor packages of this invention, the amount of Th can be further decreased by removing the surface layer of end faces other than the polished surface which counters. It is as follows when this point is described in detail. That is, although edges other than the polished surface which counters are usually a cutting plane or a rough ZURI side in case polish processing of the glass is carried out at the aperture material for a package, CeO2 of an abrasive material fixes to the cutting plane or a rough ZURI side, and ThO2 which is an impurity in CeO2 becomes a source of alpha rays by remaining without being washed. Then, it can prevent CeO2 fixing during polish by graduating the concavo-convex section of an edge in advance by acid treatment etc. Moreover, acid treatment etc. may remove the surface layer of an edge after polish.
[0037] As mentioned above, although the characteristic requirements for the manufacture approach of the aperture material glass for semiconductor packages of this invention have been explained, in order for both U and Th content to obtain glass of 5 or less ppb, of course, consideration which uses few [as much as possible] high grade raw materials of a radioisotope content, and radioisotope does not mix as much as possible in mixing of a raw material and migration to a fusion furnace must be carried out as the premise.

[Translation done.]

EXAMPLE

[Example] An example explains this invention in more detail below.
[0039] (Example 1) Various high grade raw materials were used, and the raw material batch was produced so that it might become the presentation of a table 1 of No.1. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.8ppb and 3.2ppb, respectively. It melted and refined in 1480 degrees C and 8 hours, having put this raw material batch (it being 10kg by oxide conversion) into the crucible made from platinum of 5l. capacity, having flowed N2 gas by the flow rate of 40l. / min all over the kanthal super furnace (molybdenum silicide heating element activity), and intercepting raw materials for glass with a fusion furnace ambient atmosphere (degassing, homogenization). It cast to the iron metal flask, predetermined annealing was carried out, and the glass block (henceforth Glass A) was obtained. When U of this glass A and Th content were analyzed using TCP-MASS by YOKOGAWA ELECTRIC CORP., it was 2.5ppb and 3.4ppb, respectively, and both U and Th content were 5 or less ppb.
[0040] (Example 1 of a comparison) Except not carrying out the inflow of N2 gas, it is the same conditions as an example 1, and the glass block (henceforth comparison glass V) was obtained similarly. U of this comparison glass V and Th content were 42ppb and 3.6ppb, respectively, and its U content was remarkably high compared with the example 1.
[0041] From the result of an example 1 and the example 1 of a comparison, it became clear by N2 gas's permuting a furnace atmosphere and intercepting glass from a furnace atmosphere that U content could be decreased notably.
[0042] (Example 2) The raw material batch was produced using the high grade raw material so that it might become the presentation of a table 1 of No.4. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.2ppb and 0.1ppb, respectively. As shown in drawing 3 for the heating dissolution of glass, it consisted of outer wall material 12 and a silicon carbide heating element 13, the wall 14 was divided with the silica block, and the electric furnace 15 made into muffle structure was used. The contents of U and Th of the outer wall material 12 (nature brick of a chamotte) of a wall 14 (silica block) and an electric furnace were U:19ppb, Th:0.1ppb and U:30 ppm, and Th:55ppm, respectively. The crucible made from platinum of 1l. capacity was used, it melted, the raw material batch (it is 2kg by oxide conversion) was refined in 1430 degrees C and 6 hours, it cast to the iron metal flask, predetermined annealing was carried out, and the glass block (henceforth Glass B) was obtained. When this glass B was analyzed, the contents of U and Th were 1.2ppb and 0.2ppb, respectively.
[0043] (Example 2 of a comparison) Except having used the electric furnace which removed the wall of the silica block 14 of drawing 3 , it is the same conditions as an example 2, and the glass block (henceforth comparison glass W) was obtained similarly. The analysis values of U and Th of this comparison glass W were 18ppb and 0.3ppb, respectively.
[0044] From the result of an example 2 and the example 2 of a comparison, it became clear by constituting the part in contact with a furnace atmosphere from an ingredient with few radioisotope contents, and intercepting glass from a furnace atmosphere that U content in glass could be decreased.
[0045] (Example 3) Polish processing of the glass A obtained in the example 1 was carried out by the usual approach, and the aperture material glass for a package (henceforth Glass C) of a predetermined configuration (15.5x17.7x0.8mm) was produced. Although 15.5x17.7mm side of this glass C is a ground field, 15.5x0.8mm side and 17.7x0.8mm side are cutting planes which had the angle beveled. After having applied the protective coat to the polished surface, being immersed in the fluoric acid water solution and etching only an end face, the protective coat was removed and glass (henceforth Glass D) was obtained. U of the glass C before etching and Th analysis value were U:2.5ppb and Th:5.8ppb, respectively, and U of the glass D after etching and Th analysis value were U:2.3ppb and Th:3.8ppb, respectively. That is, it became clear by removing the rough ZURI side of an edge that Th of a polish article could be decreased.
[0046] (Example 4) Various high grade raw materials were used so that it might become the presentation of a table 2 of No.1, and the raw material batch was produced. The amount of U and Th contained in this raw material batch was calculated from the amount of impurities of U and Th contained in each raw material, and were 0.7ppb and 0.4ppb, respectively. With the muffle furnace of drawing 3 , it rough-melted in 1350 degrees C and 3 hours using the silica crucible of 7l. capacity, and it melted and it was refined in 1350 more degrees C and 5 hours after moving and changing this raw material batch (it is 12kg by oxide conversion) into the crucible made from platinum of 5l.

capacity. It cast to the iron metal flask, predetermined annealing was carried out, and the glass block was obtained. After carrying out polish processing of this glass with a conventional method, the end face was removed like the example 3 and the 15.5x17.7x2.0mm aperture material glass for a package (henceforth Glass E) was obtained. The analysis values of U and Th of this glass E were 1.9ppb and 0.8ppb, respectively. Moreover, the spectral transmittance of this glass E had the near-infrared light cut property suitable as an object for CCD correction by sensitiveness, as shown in drawing 4 .

[0047] (Example of a trial) Epoxy resin adhesive was used and sealed using the polish plate and Glass D, and E itself which carried out polish processing with the conventional method, and obtained Glass A and B as aperture material glass for a package in the alumina ceramic package which contained the CCD chip of 580,000 pixels of effective pixel numbers for these, and the solid state image pickup device was produced.

[0048] The solid state image pickup device was similarly produced using the glass which carried out polish processing with the conventional method, and obtained the commercial aperture material glass for a package (henceforth comparison glass X) as aperture material glass for a package for the comparison.

[0049] In addition, although it was going to produce to the solid state image pickup device using the commercial near-infrared absorption glass for correction by sensitiveness (it is called FUTSU phosphate glass and following comparison glass Y), this comparison glass Y had the coefficient of thermal expansion as large as 158x10-7K-1, and when it was sealing, the crack occurred and it was not able to obtain a solid state image pickup device.

[0050] Next, these obtained solid state image pickup devices were used, and the existence of a soft error was investigated. The result is shown in a table 3. In addition, the alpha-rays burst size was measured among the table with the alpha-rays measuring device LACS by the Sumitomo analysis pin center,large company. When using the glass by this invention so that clearly from a table 3, it became clear that a soft error could be reduced greatly.

[0051] It cannot be overemphasized that this invention is not limited to the above-mentioned example, and various variations may exist as mentioned above.

[0052] A weight % display shows the various glass presentations which can be used for a table 1 and a table 2 in this invention. A coefficient of thermal expansion is the measured value by the TMA analysis apparatus among a table. All have the coefficient of thermal expansion which suited sealing with an alumina ceramic.

[0053]

[A table 1]

(ホウケイ酸ガラス)

No.	1	2	3	4	5	6	7	8
SiO_2	69.4	65.4	69.4	59.0	67.8	67.3	61.4	74.5
B_2O_3	17.6	17.6	15.0	20.0	15.8	15.8	17.8	6.3
Al_2O_3	3.6	3.6		3.0	2.5	3.1	1.6	6.6
Li_2O	0.7	0.7						
Na_2O	0.7	0.7	10.0		4.3	10.7		6.2
K_2O	8.0	8.0	1.6	15.4	8.1		7.2	1.3
BaO					1.3			5.1
ZnO		4.0	4.0	2.6	0.2	3.1	10.0	
NaCl							2.0	
Sb_2O_3	1.0	1.0	0.4	0.2	0.2	0.2		0.4
熱膨張係数 ($x10^{-7}K^{-1}$)	48	60	67	72	65	64	47	55

[0054]

[A table 2]

（CuO含有、P_2O_5－Al_2O_3ベースガラス）

No.	1	2	3	4	5	6	7
P_2O_5	76.3	71.4	77.7	73.2	80.5	57.0	65.0
Al_2O_3	14.5	9.0	15.0	12.1	7.7	15.0	15.0
B_2O_3	1.0					5.0	10.0
SiO_2					5.2	23.0	10.0
MgO	5.2	4.5	4.3				
CaO				6.7			
SrO				2.0			
BaO		5.3	3.0		6.6		
ZnO	1.0	8.0					
Sb_2O_3				6.0			
Nb_2O_5		1.8					
CuO	2.0	2.6	4.0	1.0	0.6	0.6	0.4
熱膨張係数 ($\times10^{-7}K^{-1}$)	67	68	62	69	72	52	57

[0055]
[A table 3]

	U 量 (ppb)	Th量 (ppb)	α線放出量 (c/cm²・hr)	ソフトエラー
ガラス A	2.5	3.4	< 0.0015	少ない
ガラス B	1.2	0.2	< 0.0015	少ない
ガラス C	2.3	3.8	< 0.0015	少ない
ガラス D	1.9	0.8	< 0.0015	少ない
比較ガラスV	42	3.6	0.004	非常に多い
比較ガラスW	18	0.3	0.002	非常に多い
比較ガラスX	12	13	0.002	多い
比較ガラスY	210	93	0.02	—

[Translation done.]

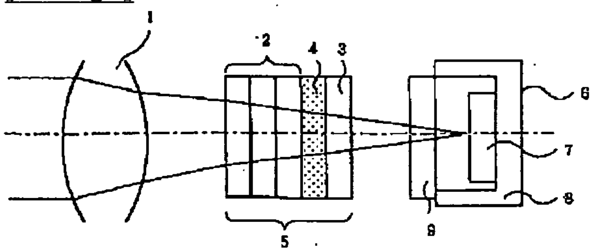
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the explanatory view showing the configuration of the optical system of a VTR camera.
[Drawing 2] It is the explanatory view showing the configuration of the optical system of the VTR camera using the aperture material glass for semiconductor packages which consists of near-infrared absorption glass of this invention.
[Drawing 3] It is the explanatory view showing the cross section of the electric furnace used for melting glass in an example.
[Drawing 4] The spectral transmittance curve of the aperture material glass for semiconductor packages which consists of near-infrared absorption glass of this invention is shown.
[Description of Notations]
1 Lens System
2 Three Quartz plate
4 Near-infrared Absorption Filter
6 Ten Solid state image pickup device
7 CCD Chip
8 Alumina Ceramic Package
9 Aperture Material for Package
11 Filter for Protection
12 Outer Wall Material
13 Silicon Carbide Heating Element
14 Wall
15 Electric Furnace

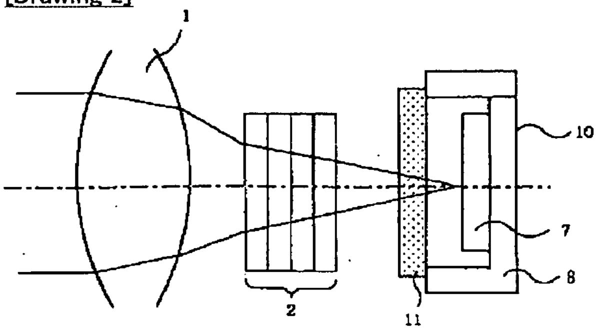
[Translation done.]

DRAWINGS

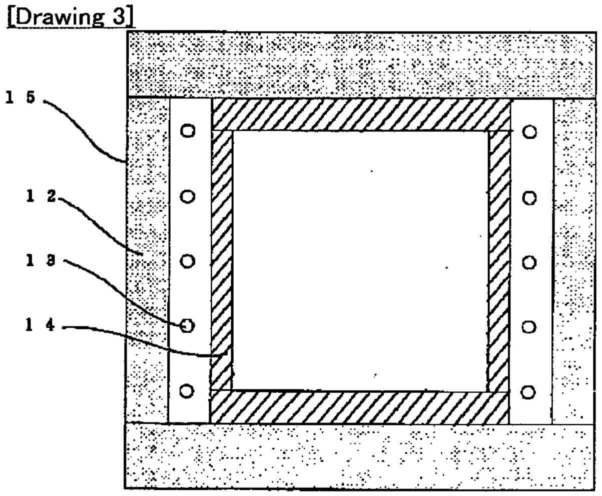
[Drawing 1]



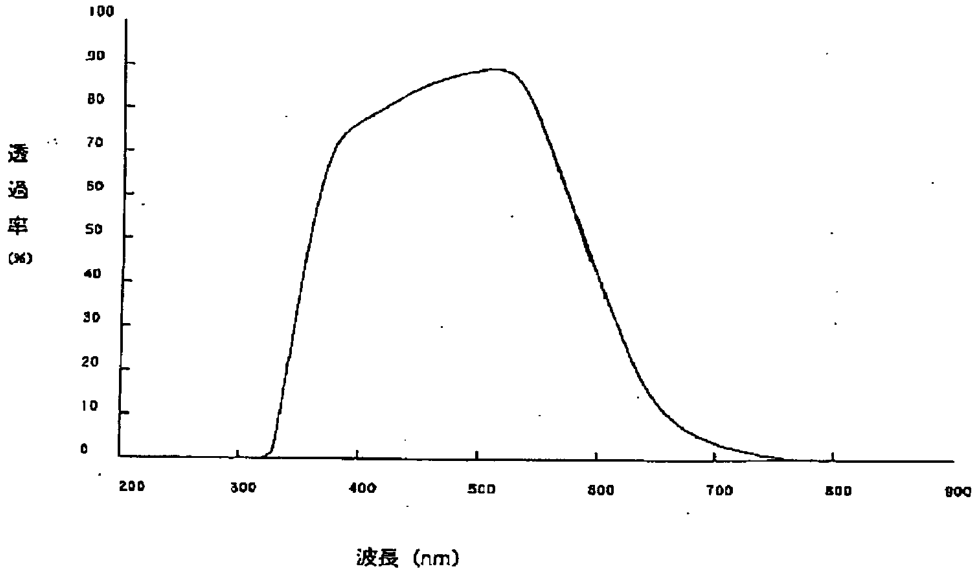
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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3/089			3/089	
3/091			3/091	
3/093			3/093	

審査請求　未請求　請求項の数８　ＯＬ　（全１０頁）　最終頁に続く

(21)出願番号　特願平７－１０５２７１

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(54)【発明の名称】半導体パッケージ用窓材ガラス及びその製造方法

(57)【要約】
【目的】　α線の主な発生源となるＵ及びＴｈのガラスへの混入が抑制できる半導体パッケージ窓材用ガラスを提供する。
【構成】　Ｕ及びＴｈの含有量が共に５ｐｐｂ以下であることを特徴とする半導体パッケージ用窓材ガラス。

【特許請求の範囲】
【請求項１】　Ｕ及びＴｈの含有量が共に５ｐｐｂ以下であることを特徴とする半導体パッケージ用窓材ガラス。
【請求項２】　重量％で、SiO_2を５０～７８％、B_2O_3を５～２５％、Al_2O_3を０～８％、Li_2Oを０～５％、Na_2Oを０～１８％及びK_2Oを０～２０％（但し、$Li_2O+Na_2O+K_2O$を５～２０％）含有し、上記成分の含有量が少なくとも８０％以上であり、熱膨張係数が$45\sim75\times10^{-7}K^{-1}$であるホウケイ酸ガラスからなる、請求項１に記載の半導体パッケージ用窓材ガラス。
【請求項３】　重量％で、P_2O_5を５０～８５％およびAl_2O_3を４～２０％含有し、両者の合計が６３％以上であり、ＣｕＯを０．１～１０％含有し、かつ熱膨張係数が$45\sim78\times10^{-7}K^{-1}$である近赤外吸収ガラスからなる、請求項１に記載の半導体パッケージ用窓材ガラス。
【請求項４】　熔解ガラスの表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断した状態でガラスを熔解することを特徴とする半導体パッケージ用窓材ガラスの製造方法。
【請求項５】　（ａ）熔解炉内の熔融ガラスの表面の全部又は一部を遮断ガスで覆う方法、
（ｂ）熔解炉内の熔融ガラスの表面の全部又は一部を白金製及び／又は放射性同位元素含有量の少ないセラミック製の蓋で覆う方法、
（ｃ）熔解炉内雰囲気に接触する内壁部分が白金及び／又は放射性同位元素含有量の少ないセラミックスで構成されている熔解炉を用いる方法、から選ばれる少なくとも１つの方法によって行なう、請求項４に記載の方法。
【請求項６】　ガラスの研磨面以外の端部の表面層を除去する、請求項４又は５に記載の方法。
【請求項７】　請求項１～３のいずれか一項に記載の半導体パッケージ用窓材ガラスを装着して成る固体撮像素子。
【請求項８】　請求項４～６のいずれか一項に記載の方法により得られた半導体窓材用ガラスを装着して成る固体撮像素子。

【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は、半導体パッケージ用窓材ガラス及びその製造方法に関し、詳しくはビデオカメラなどに使用されるＣＣＤ（固体撮像素子）などの半導体パッケージ用窓材として使用されるガラス及びその製造方法に関する。
【０００２】
【従来の技術】ＣＣＤ等の半導体は、パッケージ用窓材から放出されるα線によりソフトエラーを生じるため、パッケージ用窓材に含有されるα線を放出する放射線同位元素の量の低減が行われている。放射線同位元素としては、代表的にはウラン（Ｕ）、トリウム（Ｔｈ）及びラジウム（Ｒａ）が挙げられるが、Ｒａは存在量が少ないので通常は問題にされず、Ｕ及びＴｈが問題とされている。特にＵはα線放出量が多く、Ｔｈに比べて５～１０倍程度多い。従って、半導体の周辺材料におけるα線放出量の低減には、特にＵの含有量の低減が重要とされている。
【０００３】その為、固体撮像素子に照射されるα線量を低減することを目的として、既に幾つかの提案が成されている。例えば特開平３－７４８７４号公報には、センサー部に鉛を含むシリケートガラス薄膜を形成して放射線を遮断したことを特徴とする固体撮像素子が提案されている。しかし、この固体撮像素子の製造においては、シリケートガラス薄膜の製膜工程が複雑であり、長時間を要すると共にコスト高である。
【０００４】一方、特開平５－２７５０７４号公報には、放射性同位元素の含有量が１００ｐｐｂ以下、α線放出量０．０５ｃ／cm^2・ｈｒ以下であり、α線放射性元素の精製分離が困難なFe_2O_3、TiO_2、ＰｂＯ、ZrO_2を含まないガラスが提案されており、実施例には、α線放出量０．０８～０．００５ｃ／cm^2・ｈｒのガラスが開示されている。又、特開平６－２１１５３９号公報には、ＵとＴｈの含有量の多いZrO_2、ＢａＯを含まず、β線発生の原因になるK_2Oをも含まない低放射線ガラスが提案されており、実施例に、α線放出量０．００８～０．００２ｃ／cm^2・ｈｒのガラスが開示されている。
【０００５】
【発明が解決しようとする課題】しかしながら、近年、固体撮像素子の高密度化に伴って、α線によるノイズやソフトエラーが益々大きな画質向上の障害になっている。そのため、α線放出量の低減化の要求はさらに厳しくなっており、最近では、０．００１５ｃ／cm^2・ｈｒ以下が目標とされるに至っている。しかし、この目標を達成するためには、α線放出量が多いＵの含有量が５ｐｐｂを越えるガラスでは、実質的に不可能であった。
【０００６】ところで、半導体パッケージ用窓材ガラスは、アルミナセラミックパッケージと封着した時、割れや歪みが発生しない材料であることが要求される。カラーＶＴＲカメラの光学系は、図１に示すように、映像を結像させるレンズ系１と、ローパスフィルターとして作用する水晶板２、３と感度補正作用を有する近赤外吸収フィルター４を貼り合わせた素子５と、固体撮像素子６とで構成される。固体撮像素子６はその受光面に三色モザイクフィルターを形成したＣＣＤチップ７をアルミナパッケージ８にセットし、その上に保護用光透過部材であるガラス製パッケージ用窓材９をエポキシ樹脂などで接着した構成になっている。そのため、ガラス製パッケージ用窓材９とアルミナセラミックパッケージ８の熱膨

張係数を整合させることが必要である。アルミナセラミックの熱膨張係数は通常６０～７５×$10^{-7}K^{-1}$の範囲にあり、ガラスの熱膨張係数は、これと同等か、若干小さな４５～７５×$10^{-7}K^{-1}$の範囲であることが望ましい。ＣＣＤの感度領域は可視光域から近赤外光域に亘っている。そのため、近赤外吸収フィルターを用いて入射光の近赤外部分をカットし、総合して得られる感度を視感度に近似させ、色再現性を改善することが必要であり、図１に示すように素子５には近赤外吸収フィルター４が３枚の水晶板２と１枚の水晶板３の間に組み込まれており、素子５を構成する層数が多く、その製造コストが高いという欠点があった。

【０００７】従って本発明の目的は、(i) Ｕ及びＴｈの含有量が少なく、固体撮像素子のソフトエラーの発生を抑制でき、画質の向上に寄与できる、(ii) アルミナパッケージと熱膨張係数が整合されており、アルミナパッケージとの封着性に優れているという利点を有し、必要に応じて(iii) 感度補正機能を併有し、装置の小型化、コスト削減を達成し得るなどの利点も有する半導体パッケージ用窓材ガラス及びその製造方法を提供することにある。

【０００８】

【課題を解決するための手段】これまで、ガラスに含まれる放射能同位元素は、ガラスの原料に起因するものが殆どであると考えられていた。しかるに、本発明者が、ガラスの原料として放射性同位元素含有量が極めて少ない高純度のものを用いてガラスを試作したところ、得られたガラスの放射性同位元素含有量は依然として高いレベルであることを見い出した。即ち、ガラスに含まれる放射性同位元素の低減には、ガラスの原料を厳選する以外に、ガラス製造過程での混入を抑制する必要があることが判明した。そしてガラス製造過程での放射性同位元素の混入を防止する具体的手段として、熔融ガラスの表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断した状態でガラスを熔解することにより、得られたガラスが５ｐｐｂ以下のＵ含有量及び５ｐｐｂ以下のＴｈ含有量を有し、その結果α線放出量が０．００１５ｃ／cm^2・ｈｒ以下となり、半導体パッケージ用窓材ガラスとして好適であることを見い出した。

【０００９】本発明は、このような知見に基づいて完成されたものであり、本発明は、（Ｉ）Ｕ及びＴｈの含有量が共に５ｐｐｂ以下であることを特徴とする半導体パッケージ用窓材ガラス、および（II）熔解ガラスの表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断した状態でガラスを熔解することを特徴とする半導体パッケージ用窓材ガラスの製造方法を要旨とする。

【００１０】(Ｉ) 半導体パッケージ用窓材ガラス

先ず本発明の半導体パッケージ用窓材ガラスについて説明する。

【００１１】本発明の半導体パッケージ用窓材ガラスは、Ｕ及びＴｈの含有量が共に５ｐｐｂ以下である。従来の半導体パッケージ用窓材ガラスとしては、Ｕ含有量が５ｐｐｂを越えるものしか得られておらず、この点で本発明の半導体パッケージ用窓材ガラスは従来存在しなかった新規なガラスである。このようなＵ及びＴｈの含有量が共に５ｐｐｂ以下と極めて少ない本発明の半導体パッケージ用窓材ガラスは、Ｕ及びＴｈの含有量が極めて少ない結果としてα線放出量が０．００１５ｃ／cm^2・ｈｒ以下と極めて低く、固体撮像素子に用いたときにソフトエラー率を著しく低減できる。

【００１２】本発明の半導体パッケージ用窓材ガラスにおいて、Ｕ及びＴｈの含有量は共に３ｐｐｂ以下が好ましく、α線放出量は０．００１ｃ／cm^2・ｈｒ以下が好ましい。

【００１３】本発明の半導体パッケージ用窓材ガラスの材料としては、ホウケイ酸ガラスまたはＣｕＯを含有し、P_2O_5－Al_2O_3をベースとする近赤外吸収ガラスが挙げられる。

【００１４】本発明のガラス材料の一態様である上記ホウケイ酸ガラスは、好ましくは重量％でSiO_2を５０～７８％、B_2O_3を５～２５％、Al_2O_3を０～８％、Li_2Oを０～５％、Na_2Oを０～１８％及びK_2Oを０～２０％（但し、Li_2O＋Na_2O＋K_2Oを５～２０％）含有し、上記成分の含有量が少なくとも８０％以上であり、熱膨張係数が４５～７５×$10^{-7}K^{-1}$であるものが好ましい。

【００１５】以下にこのホウケイ酸ガラスにおける各成分の作用及び組成限定理由を説明する。

【００１６】SiO_2とB_2O_3はホウケイ酸ガラスの骨格を作る成分である。SiO_2が５０％未満となり、B_2O_3が２５％を越えると耐候性が低下する傾向がある。また、SiO_2が７８％を越え、B_2O_3が５％未満では熔融性が悪化する傾向がある。従って、SiO_2は５０～７８％の範囲にあり、かつB_2O_3は５～２５％の範囲であることが適当である。

【００１７】Al_2O_3はガラスの耐候性を向上させる成分である。しかし、８％を越えるとガラス内に脈理が発生し易くなる傾向がある。従って、Al_2O_3の含有量は８％以下とすることが適当である。

【００１８】Li_2O、Na_2O及びK_2Oは融剤として作用し、かつ、耐失透性を良くする成分である。そのためには、これらの成分の１種又は２種以上の合計の含有量は５％以上が適当である。しかし、これらの成分の１種又は２種以上の合計の含有量が２０％を越えると耐候性が悪くなり、かつ熱膨張係数が大きく成りすぎる傾向がある。さらにこれらの成分の内、Li_2Oは、多量に添加すると耐失透性が悪化する傾向があり、かつ耐火物の容器を浸食する作用も強い。そのため、Li_2Oの含有量は５％以下にすることが好ましい。Na_2O及びK_2Oは、それぞれ１８％及び２０％を越えると耐候性が悪

化し、かつ熱膨張係数も大きくなりすぎる傾向がある。そのため、Na_2O及びK_2Oの含有量は、それぞれ１８％以下及び２０％以下とすることが好ましい。

【００１９】以上の成分の他に、耐候性、熔融性、耐失透性の改善や、熱膨張係数の調整等の目的で２０％以内の範囲で、アルカリ土類金属酸化物（MgO，CaO，SrO，BaO）、ZnO、Cl等のハロゲン等を添加することも可能である。更に、As_2O_3、Sb_2O_3等の脱泡剤も必要に応じて適宜添加することができる。又、その他の３価以上の高原子価金属酸化物も所望の特性を損なわない程度に添加することが可能である。

【００２０】本発明ガラス材料のもう１つの態様である、CuOを含有し、$P_2O_5-Al_2O_3$をベースとする近赤外吸収ガラスは、好ましくは重量％で、P_2O_5を５０～８５％及びAl_2O_3を４～２０％含有し、両者の合計が６３％以上であり、CuOを０．１～１０％含有し、かつ熱膨張係数が$45\sim75\times10^{-7}K^{-1}$であるものが好ましい。この$CuO$含有、$P_2O_5-Al_2O_3$ベースの近赤外吸収ガラスを半導体パッケージ用窓材ガラスとして用いると、近赤外吸収フィルターとしての機能も兼ねさせることができる。すなわち、図２で示すようにパッケージ用窓材ガラスとして、アルミナセラミックパッケージ８の熱膨張係数と熱膨張係数を整合させた近赤外吸収ガラス１１を用いることによって、図１に示すように近赤外吸収フィルター４を水晶板２と水晶板３との間に設ける必要がなく、製品の小型化とコストダウンが可能となった。

【００２１】以下にこの近赤外吸収ガラスの各成分の作用と組成限定理由を説明する。

【００２２】P_2O_5は可視光の透過率が高く、近赤外光のカット性がよく、感度補正用として好適なガラスを得るために必須な成分である。しかし、８５％を越えるとガラスの粘性が高くなりすぎる傾向があると共に、揮発も激しくなり、熔融が困難になるので、上限は８５％、好ましくは８０％である。一方、P_2O_5が５０％未満では熱膨張係数が大きくなりすぎる傾向があるので、下限は５０％、好ましくは５５％である。

【００２３】Al_2O_3は、化学的耐久性を改善するのに特に効果的な成分である。しかし、４％未満ではその効果が充分でなく、２０％を越えると耐失透性が悪化する傾向がある。そこで、下限は４％、好ましくは７％であり、上限は２０％、好ましくは１５％である。

【００２４】CuOの含有量は０．１～１０％、好ましくは０．１～６％である。CuOは、近赤外光カットに有効であるが、０．１％未満ではその効果が少なく、１０％を越えると耐失透性と共に可視光の透過率が悪化する傾向がある。

【００２５】さらに、B_2O_3の含有量が０～１５％であり、SiO_2の含有量が０～２５％であり、MgO，CaO，SrO，BaO及びZnOからなる群の１種又は２種以上の含有量が０～２５％であり、B_2O_3、SiO_2、MgO，CaO，SrO，BaO及びZnOからなる群の１種又は２種以上の含有量が５～３７％であり、かつ、P_2O_5、Al_2O_3、B_2O_3、SiO_2、MgO，CaO，SrO，BaO及びZnOからなる群の含有量の合計が８５％以上であることが好ましい。

【００２６】SiO_2、B_2O_3は耐失透性の改善や熱膨張係数を低下させるのに有効である。しかし、SiO_2は２５％を越えると難熔性になり、B_2O_3は１５％を越えると耐失透性を悪化させる傾向がある。

【００２７】MgO，CaO，SrO，BaO及びZnOは熔融性の改善や耐失透性の改善に有効である。しかし、２５％を越えると熱膨張係数が大きくなりすぎ、所望の熱膨張係数を得るのは困難になる。

【００２８】さらに、B_2O_3、SiO_2、MgO，CaO，SrO，BaO及びZnOからなる群の合量は、熔融性、耐失透性、熱膨張係数、透過特性という観点から、５～３７％、好ましくは６～３０％の範囲とすることが適当である。

【００２９】また、P_2O_5、Al_2O_3、B_2O_3、SiO_2、MgO，CaO，SrO，BaO及びZnOからなる群の含有量の合計は、同様の理由から８５％以上、好ましくは９０％以上であることが適当である。上記の成分以外に、耐候性、熔融性、耐失透性等の改善や熱膨張係数の調整等を目的として、１５％以内、好ましくは１０％以内の範囲で、Sb_2O_3、Nb_2O_5、PbO、La_2O_3、アルカリ金属酸化物等を含有することも可能である。

【００３０】上記のホウケイ酸ガラスおよびCuO含有、$P_2O_5-Al_2O_3$ベースガラスを形成するための原料は、水溶液、炭酸塩、硝酸塩、水酸化物、酸化物等いずれの形態でも良い。但し、前記のように、不純物として混入するＵ及びＴｈの含有量の少ない原料を選択する必要がある。

【００３１】<u>（II）半導体パッケージ用窓材ガラスの製造方法</u>

本発明の半導体パッケージ用窓材ガラスの製造方法は、熔融ガラス表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断した状態でガラスを熔融することを特徴とする。

【００３２】熔融ガラスの表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断するための方法としては、（ａ）熔解炉内の熔融ガラスの表面の全部又は一部を遮断ガスで覆う方法、（ｂ）熔解炉内の熔融ガラスの表面の全部又は一部を白金製及び／又は放射性同位元素含有量の少ないセラミック製の蓋で覆う方法、（ｃ）熔解炉内雰囲気に接触する内壁部分が白金及び／又は放射性同位元素含有量の少ないセラミックスで構成されている熔解炉を用いる方法

上記方法（ａ），（ｂ）または（ｃ）を採用することに

より、U及びTh含有量が極めて少ないガラスが得られる理由は、以下のように推測される。すなわち、ガラスの熔解操作において、熔解炉の内壁を構成するレンガや発熱体（例えば炭化珪素焼結体やモリブデンシリサイド焼結体）から放射性同位元素、特にUの蒸気が発生するが、上記方法（a）～（c）の少なくとも1つによって、ガラス表面の全部又は一部が熔解炉内雰囲気と接触するのを遮断すると、U蒸気がガラス中に混入するのが防止される。

【0033】本発明の方法は、上記方法（a），（b）および（c）のいずれかを採用することにより行なっても良く、また上記方法（a）または方法（b）と、方法（c）とを併用してもよい。

【0034】上記方法（a）で用いる遮断ガスとしては、ガラスと溶解炉雰囲気とが接触するのを防止でき、かつガラスに対して実質的に不活性なものであれば、その種類は問わないが、例えばN_2、Ar、空気、炭酸ガス、CH_4、LNGなどの炭化水素ガスなどを用いることができる。

【0035】上記方法（c）において用いる熔解炉は、放射性同位元素含有量の少ないセラミックで内壁を構成したマッフル炉を用いるのが好ましいが、必ずしもマッフル構造でなくても良く、通常の熔解炉の内壁（天井、側壁等）を放射性同位元素含有量の少ないセラミックで構成しても効果がある。これらのセラミックとしてはU含有量が20ppm以下、好ましくは1ppm以下のアルミナ質電鋳レンガ、シリカブロック等が好適である。又、炭化珪素焼結体やモリブデンシリサイド焼結体等の抵抗発熱体の使用を抑制し、LNG等のガス加熱が望ましい。

【0036】本発明の半導体パッケージ用窓材ガラスの製造方法においては、対向する研磨面以外の端面の表面層を除去することにより、Th量を更に減少させることができる。この点を詳しく述べると以下のとおりである。すなわち、ガラスをパッケージ用窓材に研磨加工する際、通常、対向する研磨面以外の端部は、切断面又は荒ズリ面であるが、その切断面又は荒ズリ面に研磨剤のCeO_2が固着して、洗浄されずに残存することにより、CeO_2中の不純物であるThO_2がα線源になる。そこで、端部の凹凸部を酸処理などによって事前に平滑化することにより、研磨中にCeO_2が固着するのを防ぐことができる。また研磨後、端部の表面層を酸処理等により除去しても良い。

【0037】以上、本発明の半導体パッケージ用窓材ガラスの製造方法の特徴的要件について説明してきたが、U及びTh含有量が共に5ppb以下のガラスを得るためには、その前提として放射性同位元素含有量の極力少ない高純度原料を使用し、原料の調合、熔解炉への移送において放射性同位元素が極力混入しないような配慮をしなければならないことはもちろんである。

【0038】

【実施例】以下本発明を実施例によりさらに詳しく説明する。

【0039】（実施例1）各種高純度原料を使用して、表1のNo．1の組成になるように原料バッチを作製した。この原料バッチ中に含まれるUとThの量は各原料中に含まれるUとThの不純物量から計算して、それぞれ0．8ppb及び3．2ppbであった。この原料バッチ（酸化物換算で10Kg）を、5リットル容量の白金製坩堝に入れ、カンタルスーパー炉（モリブデンシリサイド発熱体使用）中にN_2ガスを流量40リットル／minで流入して、ガラス原料を熔解炉雰囲気と遮断しながら、1480℃、8時間で熔解、精製（脱泡、均質化）した。鉄製金枠に鋳込み、所定のアニールをしてガラスブロック（以下ガラスAという）を得た。このガラスAのU及びTh含有量を横河電機（株）製TCP－MASSを用いて分析したところ、それぞれ2．5ppb及び3．4ppbであり、U及びTh含有量は共に5ppb以下であった。

【0040】（比較例1）N_2ガスの流入をしないこと以外は実施例1と同じ条件で、同様にガラスブロック（以下比較ガラスVという）を得た。この比較ガラスVのU及びTh含有量はそれぞれ42ppb及び3．6ppbであり、実施例1に比べU含有量が著しく高かった。

【0041】実施例1と比較例1の結果から、炉内雰囲気をN_2ガスで置換して、ガラスを炉内雰囲気から遮断することにより、U含有量を顕著に減少できることが判明した。

【0042】（実施例2）表1のNo．4の組成になるように高純度原料を使用して原料バッチを作製した。この原料バッチに含まれるUとThの量は、各原料に含まれるUとThの不純物量から計算して、それぞれ0．2ppb及び0．1ppbであった。ガラスの加熱熔解のために図3に示すように、外壁材12と炭化珪素発熱体13で構成され、内壁14をシリカブロックで仕切り、マッフル構造とした電気炉15を用いた。内壁14（シリカブロック）と電気炉の外壁材12（シャモット質レンガ）のUとThの含有量はそれぞれU：19ppb、Th：0．1ppb及びU：30ppm、Th：55ppmであった。原料バッチ（酸化物換算で2Kg）を1リットル容量の白金製坩堝を用いて、1430℃、6時間で熔解、精製し、鉄製金枠に鋳込み、所定のアニールをしてガラスブロック（以下ガラスBという）を得た。このガラスBを分析したところ、UとThの含有量はそれぞれ1．2ppb及び0．2ppbであった。

【0043】（比較例2）図3のシリカブロック14の内壁を取り除いた電気炉を用いたこと以外は実施例2と同じ条件で、同様にガラスブロック（以下比較ガラスWという）を得た。この比較ガラスWのUとThの分析値

はそれぞれ１８ｐｐｂ及び０．３ｐｐｂであった。

【００４４】実施例２と比較例２の結果から、炉内雰囲気に接触する部分を放射性同位元素含有量の少ない材料で構成して、ガラスを炉内雰囲気から遮断することにより、ガラス中のＵ含有量を減少できることが判明した。

【００４５】（実施例３）実施例１で得られたガラスＡを通常の方法で研磨加工し、所定形状（１５．５×１７．７×０．８ｍｍ）のパッケージ用窓材ガラス（以下ガラスＣという）を作製した。このガラスＣの１５．５×１７．７ｍｍ面は研磨された面であるが、１５．５×０．８ｍｍ面及び１７．７×０．８ｍｍ面は角を面取りされた切断面である。研磨面に保護膜を塗布し、フッ酸水溶液に浸漬して、端面のみをエッチングした後、保護膜を除去してガラス（以下ガラスＤという）を得た。エッチング前のガラスＣのＵ、Ｔｈ分析値はそれぞれＵ：２．５ｐｐｂ、Ｔｈ：５．８ｐｐｂであり、エッチング後のガラスＤのＵ、Ｔｈ分析値はそれぞれＵ：２．３ｐｐｂ、Ｔｈ：３．８ｐｐｂであった。即ち、端部の荒ズリ面を除去することによって、研磨品のＴｈを減少できることが判明した。

【００４６】（実施例４）表２のＮｏ．１の組成になるように各種高純度原料を使用して、原料バッチを作製した。この原料バッチに含まれるＵとＴｈの量は、各原料に含まれるＵとＴｈの不純物量から計算して、それぞれ０．７ｐｐｂ及び０．４ｐｐｂであった。この原料バッチ（酸化物換算で１２Ｋｇ）を図３のマッフル炉で、７リットル容量のシリカ坩堝を用いて１３５０℃、３時間で粗熔解し、５リットル容量の白金製坩堝に移し変えた後、さらに１３５０℃、５時間で熔解、精製した。鉄製金枠に鋳込み、所定のアニールをしてガラスブロックを得た。このガラスを常法により研磨加工した後、実施例３と同様にして端面を除去して１５．５×１７．７×２．０ｍｍのパッケージ用窓材ガラス（以下ガラスＥという）を得た。このガラスＥのＵ及びＴｈの分析値はそれぞれ１．９ｐｐｂ及び０．８ｐｐｂであった。又、このガラスＥの分光透過率は、図４に示すように、ＣＣＤ感度補正用として好適な近赤外光カット特性を有していた。

【００４７】（試験例）パッケージ用窓材ガラスとして、ガラスＡ，Ｂを常法により研磨加工して得た研磨板およびガラスＤ，Ｅそれ自体を用い、これらを有効画素数５８万画素のＣＣＤチップを内蔵したアルミナセラミックパッケージにエポキシ樹脂系接着剤を用いて封着し、固体撮像素子を作製した。

【００４８】比較のため、パッケージ用窓材ガラスとして、市販のパッケージ用窓材ガラス（以下比較ガラスＸという）を常法により研磨加工して得たガラスを用いて、同様に固体撮像素子を作製した。

【００４９】なお、市販の感度補正用近赤外吸収ガラス（フッ燐酸塩ガラス、以下比較ガラスＹという）を用いて固体撮像素子に作製しようとしたが、この比較ガラスＹは熱膨張係数が１５８×$10^{-7}$$K^{-1}$と大きく、封着の際、割れが発生し、固体撮像素子を得ることができなかった。

【００５０】次に、得られた、これらの固体撮像素子を使用して、ソフトエラーの有無を調査した。その結果を表３に示す。尚、表中、α線放出量は住友分析センター社製α線測定装置ＬＡＣＳで測定した。表３から明らかなように、本発明によるガラスを使用すれば、ソフトエラーを甚だしく低減できることが判明した。

【００５１】本発明は、上記の実施例に限定されるものではなく、前述のように種々のバリエーションが存在し得ることは言うまでもない。

【００５２】表１及び表２に本発明において使用し得る種々のガラス組成を重量％表示で示す。表中、熱膨張係数はＴＭＡ分析装置による測定値である。いずれも、アルミナセラミックとの封着に適合した熱膨張係数を有している。

【００５３】

【表１】

(ホウケイ酸ガラス)

No.	1	2	3	4	5	6	7	8
SiO_2	69.4	65.4	69.4	59.0	67.8	67.3	61.4	74.5
B_2O_3	17.6	17.6	15.0	20.0	15.8	15.8	17.8	6.3
Al_2O_3	3.6	3.6		3.0	2.5	3.1	1.6	6.6
Li_2O	0.7	0.7						
Na_2O	0.7	0.7	10.0		4.3	10.7		6.2
K_2O	8.0	8.0	1.6	15.4	8.1		7.2	1.3
BaO					1.3			5.1
ZnO		4.0	4.0	2.6	0.2	3.1	10.0	
NaCl							2.0	
Sb_2O_3	1.0	1.0	0.4	0.2	0.2	0.2		0.4
熱膨張係数 ($\times10^{-7}K^{-1}$)	48	50	67	72	65	64	47	55

【0054】

【表2】

13　14

（CuO含有、P_2O_5－Al_2O_3ベースガラス）

No.	1	2	3	4	5	6	7
P_2O_5	76.3	71.4	77.7	73.2	80.5	57.0	65.0
Al_2O_3	14.5	9.0	15.0	12.1	7.7	15.0	15.0
B_2O_3	1.0					5.0	10.0
SiO_2					5.2	23.0	10.0
MgO	5.2	4.5	4.3				
CaO				6.7			
SrO				2.0			
BaO		5.3	3.0		6.6		
ZnO	1.0	8.0					
Sb_2O_3				6.0			
Nb_2O_5		1.8					
CuO	2.0	2.6	4.0	1.0	0.6	0.6	0.4
熱膨張係数 ($x10^{-7}K^{-1}$)	67	68	62	69	72	52	57

【００５５】　【表３】

	U 量 (ppb)	Th量 (ppb)	α線放出量 (c/cm²·hr)	ソフトエラー
ガラス A	2.5	3.4	< 0.0015	少ない
ガラス B	1.2	0.2	< 0.0015	少ない
ガラス C	2.3	3.8	< 0.0015	少ない
ガラス D	1.9	0.8	< 0.0015	少ない
比較ガラスV	42	3.6	0.004	非常に多い
比較ガラスW	18	0.3	0.002	非常に多い
比較ガラスX	12	13	0.002	多い
比較ガラスY	210	93	0.02	—

【0056】

【発明の効果】本発明によれば、ソフトエラー率が著しく低い固体撮像素子などの半導体用のパッケージ窓材用ガラスを提供することができる。さらに、特定の組成範囲に限定することによって、アルミナセラミックパッケージと接合性の良い熱膨張係数を持つガラスを提供することができる。本発明のガラスの製造方法によれば、製造工程におけるU及びThの混入を大幅に抑制して、パッケージ用窓材に適したガラスを得ることができ、ガラスからのα線に起因するソフトエラーの発生を著しく低減できるため、固体撮像素子などの半導体の高解像度化、高密度化に貢献することができる。又、感度補正機能を持つ赤外線吸収ガラスをパッケージ用窓材として使用すれば、CCDの小型化が可能であり、コスト削減も期待できる。

【図面の簡単な説明】

【図1】VTRカメラの光学系の構成を示す説明図である。

【図2】本発明の近赤外吸収ガラスからなる半導体パッケージ用窓材ガラスを用いたVTRカメラの光学系の構成を示す説明図である。

【図3】実施例においてガラスを熔解するのに用いた電気炉の断面を示す説明図である。

【図4】本発明の近赤外吸収ガラスからなる半導体パッケージ用窓材ガラスの分光透過率曲線を示す。

【符号の説明】

1　レンズ系

2、3　水晶板

4　近赤外吸収フィルター

6、10　固体撮像素子

7　CCDチップ

8　アルミナセラミックパッケージ

9　パッケージ用窓材

11　保護用フィルター

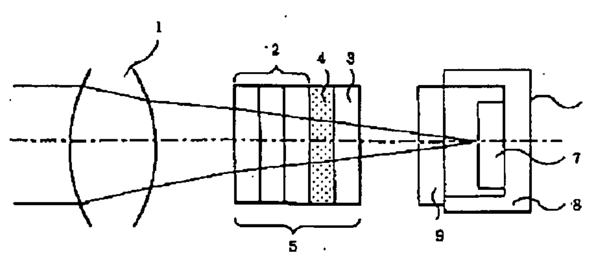
12　外壁材

13　炭化珪素発熱体

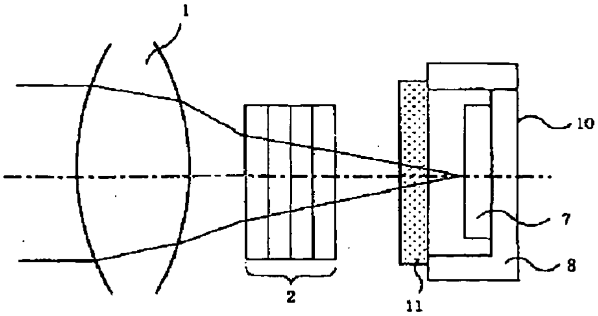
14　内壁

15　電気炉

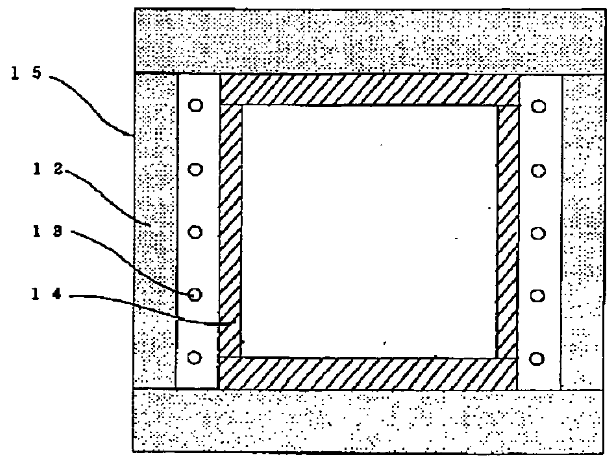
【図1】



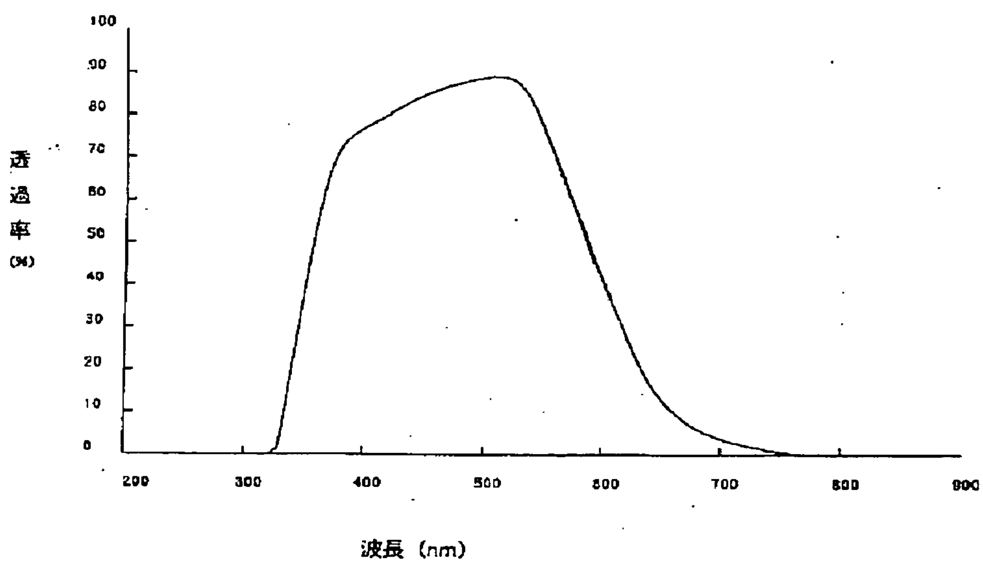
【図２】



【図３】



【図４】



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